Ab initio investigation of the ground state properties of PO, PO^+, and PO^-

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(Received 31 March 2003; accepted 18 June 2003)

We have computed accurate potential energy curves of the ground states of the $PO(X\,^2\Pi)$, $PO^+(X\,^1\Sigma^+)$ and $PO^-(X\,^3\Sigma^-)$ species by multireference configuration interaction and coupled-cluster methods and have obtained accurate spectroscopic constants for each species. We have also determined the effect of core on the properties above and have obtained the PO complete basis set limit by the multireference method for the equilibrium energy, bond distance, dissociation energy, harmonic frequency, and dipole moment. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1599341]

I. INTRODUCTION

The phosporus oxide (PO) radical and its ions have been investigated extensively by spectroscopic methods,[1–51] and, in addition to their ground states, many excited states both valence and Rydberg have been discovered. Further related references are given in many of the references cited here. The spectroscopic parameters of these species have been determined by analysis of the electronic, vibrational, and rotational spectra obtained by methods such as emission and absorption spectroscopy, vacuum ultraviolet photoelectron and laser photoelectron spectroscopy, as well as by microwave and far infrared laser magnetic resonance spectroscopy. In the present work we are interested only in some of these parameters pertaining to the ground states of PO and its ions, namely the dissociation energy, the ionization potential, ω_e, $\omega_e x_e$, μ_e, r_e, B_e, α_e, and D_e. The most accurate of these parameters have been determined by Verma and Singhal,[34] Zittel and Lineberger,[37] Petrmichl *et al.*,[50] and compiled by Huber and Herzberg[40] for works up to 1977–78. Some of these parameters have been slightly modified, while others which are missing from the early works have been later determined by other authors.[31,39,42,43,45,46,49,51] Table I shows the most recent values of these parameters. A brief history of the experimental work on PO is given by de Brouckère.[65] It is worth noting that PO is believed to exist in dense interstellar clouds although evidence of its presence there is not yet conclusive.[48]

In contrast to the experimental work, the theoretical investigation of these species has not been extensive.[52–66] The first calculations on PO and its anion were done as early as 1966 by Boyd and Lipscomb[52] at the self-consistent field/Slater type orbitals (SCF/STO) level, and their results for the PO^- were the only ones available for some time. In 1971 Mulliken and Liu[53] repeated the calculations on PO at the SCF/STO level with a larger basis set as part of their investigation of the importance of the d and f functions in the chemical bond. Ackermann *et al.*[54] calculated Rydberg states of PO at the SCF level and obtained its ionization energy. The first limited configuration interaction (CI) calculations were done in 1973 by Tseng and Grein,[55] who calculated low-lying valence states of PO with a minimal basis set of STOs. These low accuracy calculations were able to give the correct dissociation products. In the same year Roche and Lefebvre-Brion[56] published more accurate CI calculations of valence states of PO. They employed a double zeta basis set of STOs with $3d$ polarization functions on P and used the SCF molecular orbitals of each state to construct the spin-adapted functions. In 1983 Grein and Kapur[58] performed CI calculations on the ground and low-lying and Rydberg states of PO employing a double-zeta plus polarization plus diffuse functions basis set of Gaussian type orbitals (GTO) using the MRDCI package, which has the feature of approximately extrapolating the energies to their full-CI values. In 1984 Lohr[59] calculated the ground state of PO and PO^- and one excited state of PO^- as part of his study of the gaseous oxides of P. He used the MP3 and CI methods with a 6-31G* and 6-31+G* basis set optimizing the geometries at the SCF level with analytic gradient techniques using the GAUSSIAN 80 program. The first calculations of the ground state of PO^+ were done by Peterson and Woods[60] in 1988 as part of their study of 22 electron diatomics. The calculations were done at the fourth-order Møller–Plesset without triples (MP4SDQ) level of theory with a $[8s5p2d1f]$ contracted basis set on O and a $[10s7p3d1f]$ contracted basis set on P using the GAUSSIAN 82 package. The same authors did a similar study in 1990[62] using the singles and doubles CI (CISD) method with and without the Pople's size extensivity correction, but

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TABLE I. Latest experimental parameters of the ground states of PO ($X\,^2\Pi$), PO^+ ($X\,^1\Sigma^+$), and PO^- ($X\,^3\Sigma^-$) molecules. Bond distances r_e (Å), dissociation energies D_e and D_0 (eV), ionization energies I.E. (eV), harmonic and anharmonic frequencies ω_e, $\omega_e x_e$ (cm^{-1}), rotational constants B_e (cm^{-1}), rotational–vibrational couplings α_e (cm^{-1}), centrifugal distortions $\overline{D_e}$ (cm^{-1}), dipole moment μ (D),[a] and spin–orbit coupling constant A_0 (cm^{-1}).[b]

Ref./Year	Species	r_e	D_e	D_0	I.E.	ω_e	$\omega_e x_e$	B_e	$\alpha_e\times10^{-3}$	$\overline{D_e}\times10^{-6}$
31 (1974)	PO		6.22							
34 (1975)	PO					1233.34	6.56[c]	0.733 7	5.5	1.31±0.05
39 (1978)	PO			6.09	8.38					
40 (1979)	PO	1.475 9		6.15		1233.34	6.56	0.733 7	5.5	1.3
42 (1981)	PO[d]	1.475 7	6.149	6.073	8.143					
43 (1982)	PO				8.39					
45 (1983)	PO							0.730 5(B_0)		1.04
46 (1983)	PO	1.476 37	6.22[e]					0.733 23	5.4777	
47 (1983)	PO			6.175						
51 (1995)	PO							0.733 23	5.4742	1.04
40 (1979)	PO^+			8.41		1405	5			
43 (1982)	PO^+	1.419±0.005		8.25±0.01		1410±30	10±20			
50 (1991)	PO^+	1.424 99				1411.5	7.11	0.787 0		
37 (1976)	PO^-	1.54±0.01		5.78[f]	1.09±0.01	1000±70		0.699 0[g]		

[a] $\mu=1.88\pm0.07$ D, Ref. 49 (1988).
[b] $A_0=224.01\pm0.01\ cm^{-1}$, Ref. 34 (1975).
[c] $\omega_e y_e=-0.005\ cm^{-1}$.
[d] Via construction of an experimental curve.
[e] Adjusted value from D_0 of Ref. 40 using data from Ref. 46 (Woon and Dunning Ref. 63).
[f] From D_0 of PO and the electron affinities of PO and O (Ref. 40).
[g] Assuming B_0 (PO^-)/B_0 (PO)=B_e (PO^-)/B_e (PO).

with a slightly smaller basis set. A study of the ground state of PO^+ was also done by Wong and Radom[61] as part of a study of 28 isoelectronic species. Various basis sets of the 6-311G and 6-311+G type augmented with additional functions were used in calculations at the complete active space SCF (CASSCF), MP3, MP4, and coupled-cluster doubles with fourth-order perturbation correction of doubles and triples levels of theory. Woon and Dunning[63] performed benchmark calculations on several neutral diatomics including PO employing the correlation consistent basis sets of Dunning and co-workers at the CASSCF and contracted MRCI levels. Spielfiedel and Handy[64] investigated in 1999 the ground and many excited states of PO and PO^+ at both the density functional theory (DFT) and multireference CI (MRCI) levels with the CADPAC and MOLPRO codes, respectively. In the MRCI calculations the correlation consistent cc-pVQZ basis set was employed. In the same year, a study of many properties of the ground state of PO was carried out by de Brouckère[65] at the MRCI and MRCI plus Davidson correction (=+Q) levels using the aug-cc-pVQZ basis set and the MELDF-X package. Finally, in 2001 a study of multipole moments and dipole polarizabilities of the ground state of PO^+ was carried out by Martin and Fehér[66] at the CASSCF level with a $[9s6p3d1f]$ basis set on P and a $[8s6p3d1f]$ basis set on O using the GAMESS program.

Although as a total the above-mentioned calculations determined the spectroscopic parameters of interest here (*vide supra*) at varying degrees of accuracy, not all of these parameters were given in each one of the papers. Moreover, some of these parameters were estimated with different basis sets than others within the same paper. Also, the molecules were *never* opened to their asymptotic products with the exception of the CASSCF calculation of Ref. 66. Regarding the ground state of PO^-, only two parameters and its energy were given.[59] The most recent, accurate *ab initio* results are compiled in Table II.

It is the aim of this work to generate accurate and complete potential energy curves of the ground states of PO($X\,^2\Pi$), PO^+($X\,^1\Sigma^+$), and PO^-($^3\Sigma^-$), including a complete basis set (CBS) extrapolation on PO, to estimate the core effects, and to compute consistently and accurately all the above-mentioned spectroscopic parameters of the ground states of these three species.

II. METHODOLOGY

For the PO molecule the correlation consistent basis set of Dunning and co-workers was employed.[67,68] For both the P and O atoms the aug-cc-pVnZ sequence were used with $n=2$ (D), 3 (T), 4 (Q), 5 and 6 (=AnZ). The largest one electron basis, $n=6$, $(22s15p6d5f4g3h2i/_P\,16s11p6d5f4g2h2i/_O)$ contracted to $[9s8p6d5f4g3h2i/_P\,8s7p6d5f4g3h2i/_O]$, contains 382 spherical Gaussian functions. The complete active space self-consistent field plus single plus double replacements (CASSCF+1+2=MRCI) multireference approach was applied with internally contracted configurations as implemented in the MOLPRO code.[69] This code was used here for all our calculations. The zeroth-order space was defined by distributing 11 (PO), 10 (PO^+), and 12 (PO^-) "valence" (active) electrons to eight valence orbital functions (one s and three p on P, and one s and three p on O). In the MRCI calculations, the uncontracted configuration functions were about 94×10^6 for PO, 70×10^6 for PO^+, and 60×10^6 for PO^-, while the internally contracted ones were about 1.4, 1.3, and 1.2×10^6, respectively. It should be stressed at this point that all CASSCF functions obey symmetry and equivalence restrictions. The importance of these constrains is obvious if, for instance, one examines the energetics of the PO

TABLE II. Best literature *ab initio* energies and spectroscopic constants of PO ($X\,^2\Pi$), PO^+ ($X\,^1\Sigma^+$), and PO^- ($X\,^3\Sigma^-$) molecules.[a]

Ref./Year	Species	$-E$ (hartree)	r_e (Å)	D_e (eV)	I.E. (eV)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	$\alpha_e\times10^{-3}$ (cm^{-1})	$\bar{D}_e\times10^{-6}$ (cm^{-1})	μ (D)
63/1994[b]	PO	416.019 67	1.4806	5.92		1224.6	6.62	0.729	5.5		
63/1994[c]	PO	416.026 85		6.00							
64/1999[d]	PO	416.002 9	1.4870		7.91	1213.9	6.92	0.723			
64/1999[e]	PO	416.031 4	1.4891		8.24	1215.3	6.86	0.721			
65/1999[f]	PO	416.017 66	1.4808	6.23		1253.3	3.27[f]	0.7288	4.7		1.933
65/1999[g]	PO	416.037 17	1.4855			1228.9	6.58	0.7243	5.25		
60/1988[h]	PO^+	415.696 20	1.4337	8.35		1365.8	10.8		6.5	1.01	3.44[o]
61/1990[i]	PO^+	415.711 10	1.424	8.36		1378	7.2	0.76	5.2		
62/1990[j]	PO^+	415.628 19	1.4170			1518.3	5.80		4.6	0.87	3.44[o]
62/1990[k]	PO^+	415.658 11	1.4304			1439.6	6.50		5.0	0.92	
64/1999[d]	PO^+	415.712 2	1.4357		13.17	1398.7	7.33	0.775			
64/1999[e]	PO^+	415.728 5	1.4370		13.36	1391.5	7.38	0.774			
66/2001[l]	PO^+	415.468 05	1.4357	8.12		1410.4	6.8	0.7758	5.2		3.135[o]
52/1967[m]	PO^-	414.116 8	1.513								1.5[o]
59/1984[n]	PO^-	415.865 74	1.529		1.88						

[a]See Table I for symbol explanation.
[b]Contracted MRCI/cc-pV5Z.
[c]CBS values.
[d]Contracted MRCI/cc-pVQZ.
[e]MRCI+Davidson correction values (=MRCI+Q).
[f]MRCI/aug-cc-pVQZ; $\omega_e y_e = -0.14$.
[g]MRCI+Q values.
[h]MP4SDQ/$[10s7p3d1f/_P8s5p2d1f/_O]$.
[i]CASSCF-ST4CCD/6-311G (MC) (d) for spectroscopic properties-optimum geometry, but MP4/6-311G (MC) $(3d2f)$ for best energy.
[j]CISD/$[9s6p2d1f/_P7s4p2d1f/_O]$.
[k]With Pople's size extensivity correction.
[l]CASSCF/$[9s6p3d1f/_P8s6p3d1f/_O]$.
[m]SCF/Minimal basis set of Slater type orbitals.
[n]SCF/6-31G* for optimization, but MP3/6-311G* for energy.
[o]With respect to the center of mass.

ground state with and without them: at the CASSCF (MRCI)/A6Z level the $X\,^2B_1$ (or $^2B_2$) C_{2v} component is *lower* in energy by 14.6 (3.1) mhartree, as compared to the $X\,^2\Pi$ ($|\Lambda|=1$, CASSCF) state. The spectroscopic constants of the ground states of PO, PO^+, and PO^- were extracted by fitting the *ab initio* MRCI/A6Z points using cubic splines, followed by a Numerov type integration of the one-dimensional rovibrational Schrödinger equation employing a grid of about 3000 points.

For reasons of comparison we also performed calculations using the coupled-cluster+single+double excitations approach with a perturbative estimate of the connected triples out of a restricted Hartree–Fock reference wave function, RHF-RCCSD(T). The A6Z basis set was employed here as well, and enough points were obtained to enable us to calculate spectroscopic constants.

In all other calculations described in the following, involving either MRCI or RCCSD(T) with core excitations [C-MRCI, C-RCCSD(T)], only computations at a few points at large interatomic distances and around the equilibrium position were done in order to obtain the equilibrium energy, the D_e and the r_e. Each equilibrium position and energy was obtained by a fourth-order Lagrangian interpolation involving five points around the minimum and by a final calculation. The small number of *ab initio* points in these cases allowed only the estimate of ω_e, and this was done by the Dunham method.[70] The effect of the core correlation [C-MRCI, C-RCCSD(T)] was estimated in all three species by allowing "core" ($2s^22p^6$) excitations from the P atom only. Since at the moment there is no basis set of P optimized for core excitations, we had to use the A6Z set as before.

To obtain the complete basis set (CBS) limits on PO for its equilibrium energy, D_e, ω_e, r_e, and μ, we performed a series of MRCI calculations using the AnZ basis sets (n = D, T, Q, 5, 6). We ran two sets of calculations: One including corrections for the basis set superposition error (BSSE), and one without them. The resulting two CBS limits gave an estimate of the effect of the BSSE on this limit. A similar series of calculations were done for PO including core excitations (C-MRCI) but without corrections for BSSE due to the long CPU times required and due to the small effect the BSSE has on these limits (*vide infra*). All CBS limits were obtained by applying the mixed Gaussian/exponential relation:[63]

$$P(n) = P + A\exp[-(n-1)] + B\exp[-(n-1)^2],$$

where $P(n)$ is a generic property, P is its CBS limit, n is the cardinal basis set number, and A, B are freely adjusted parameters.

The spin–orbit coupling constant A_e was also obtained for the $X\,^2\Pi$ PO state, by calculating the Breit–Pauli matrix element within the MRCI-uncontracted A5Z wave function but with the g and h basis functions removed.

At this point we would like to point out two things: the deterioration of the quality of the C-MRCI wave functions due to size-nonextensivity effects, and the lack of axial symmetry of the RCCSD(T) wave functions even for the Σ states when using C_{2v} symmetry due to mixing of A_1 components of higher angular momentum states.

III. RESULTS AND DISCUSSION

The PO($X\,^2\Pi$), PO^+($X\,^1\Sigma^+$), and PO^-($^3\Sigma^-$) PECs at the MRCI and RCCSD(T)/A6Z level of theory are presented in Fig. 1. These calculations did not include BSSE corrections since these corrections are very small for the employed

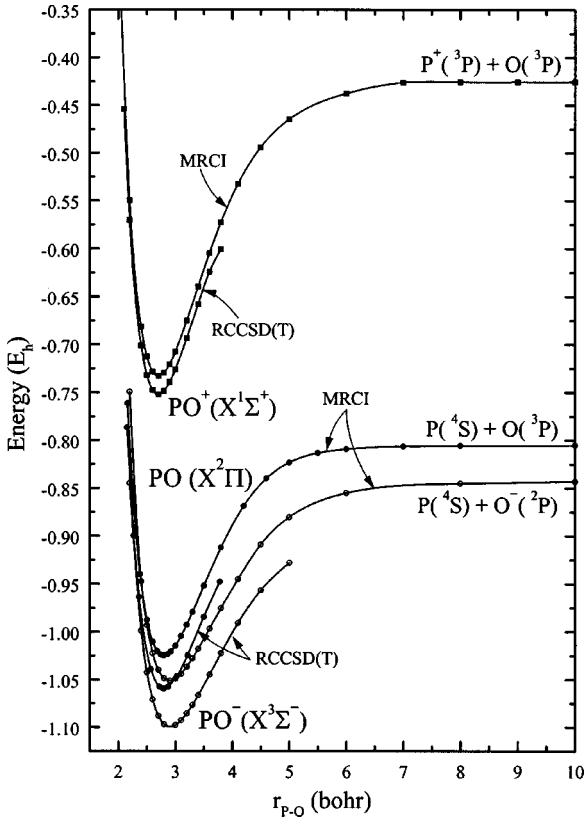


FIG. 1. Potential energy curves of PO($X\,^2\Pi$), $PO^+(X\,^1\Sigma^+)$, and $PO^-(^3\Sigma^-)$ at the MRCI and RCCSD(T)/aug-cc-pV6Z level of theory. All energies are upshifted by 415.0 hartree.

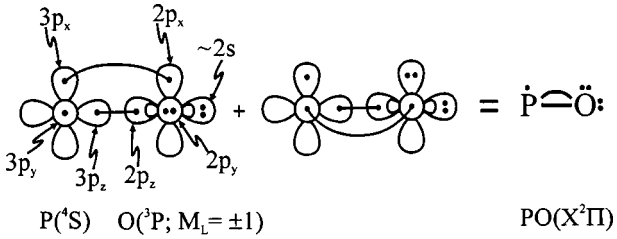
A6Z basis set (*vide infra*). The spectroscopic constants obtained using these PECs as well as some constants from the C-MRCI and C-RCCSD(T) calculations are given in Tables III (with CBS limits), IV, and V for the PO, PO^+, and PO^- species, respectively. To facilitate comparisons, the best experimental values from Table I are also included in these tables.

The sequence of MRCI, C-MRCI calculations for PO($X\,^2\Pi$) with the correlation consistent basis sets of increasing order lead to the estimate of the MRCI CBS limit for the properties r_e, D_e, ω_e, μ, and the results are presented in Table VI. The BSSE itself is given in the last column, and one can see that it is very small for the A6Z set. As a matter of fact, it is observed that it follows quite satisfactorily the expression, $\mathrm{BSSE(A}n\mathrm{Z)} = \mathrm{BSSE(A2Z)}/2^{n-2}$, $n = 2, 3, 4, 5, 6$. Therefore, it becomes practically zero (smaller than 0.05 kcal/mol) for $n = 8$. Also, the CBS values show that the effect of BSSE on the CBS limit is minimal. In the C-MRCI sequence the equilibrium energies and other properties were not changing monotonically, probably because we were using the core ($\sim 2s^2 2p^6$) without a core-optimized basis set, or because the C-MRCI values have not been corrected for BSSE, and so their CBS limit could not be obtained. An exception to this was the CBS limit of D_e.

To verify the validity of the mixed Gaussian/exponential formula used for obtaining the CBS limits for some properties, we estimated P, A, and B for each property by using the first four basis sets ($n = 2, 3, 4, 5$). Then we plotted the $P(n)$ function and obtained a $P(6)$ value very close to the *ab initio* one corresponding to the A6Z set for the concerned property.

A. PO($X\,^2\Pi$)

At the equilibrium, the bonding on the ground state of PO is represented succinctly by the following valence-bond-Lewis (vbL) diagrams:



suggesting that the two atoms are held together by two bonds, one σ and one π, and the symmetry defining electron localized on the P atom. The dominant CASSCF equilibrium configuration and Mulliken populations (P/O) are

$$|X\,^2\Pi\rangle \simeq 0.98|5\sigma^2 6\sigma^2 7\sigma^2 2\pi_x^2 2\pi_y^2 3\pi_x^1\rangle \quad (B_1 \text{ component})$$

$$3s^{1.81}3p_z^{0.78}3p_x^{1.22}3p_y^{0.61}3d_{z^2}^{0.07}3d_{xz}^{0.08}3d_{yx}^{0.08}/$$

$$2s^{1.86}2p_z^{1.43}2p_x^{1.66}2p_y^{1.33}$$

and they corroborate the above vbL picture, indicating also a net transfer of about $0.3\,e^-$ from P to O.

In contrast to the coupled cluster approach, we observe from Table III the difficulties encountered by the MRCI method in obtaining a very accurate D_e value mainly due to the size nonextensivity errors. This is rather clear from the significantly improved D_e values at the MRCI+Q, C-MRCI+Q levels of theory. Our C-MRCI(+Q) and C-RCCSD(T) D_e values indicate that the ''true'' dissociation energy of PO($X\,^2\Pi$) is closer to 143 kcal/mol if one takes into account that the coupled cluster method overestimates slightly the dissociation energy due to its inherent symmetry problem. At the C-RCCSD(T) and MRCI/CBS levels we can claim that the bond distance is in excellent agreement with the experiment, the former underestimating r_e by 0.0014 Å and the latter overestimating it by 0.0022 Å. For the harmonic frequency ω_e both MRCI/CBS and RCCSD(T) are in excellent agreement with the experimental value, but this is not so for the C-MRCI and C-RCCSD(T) results. In perfect agreement with the experiment is also the MRCI dipole moment, but the C-MRCI value deviates from the experimental value by -0.10 D, not unexpected in the light of the previous discussion. Finally, the size nonextensivity errors, particularly in the C-MRCI approach, are clearly projected in the calculation of I.E. and E.A., whereas the coupled cluster method gives excellent results.

B. $PO^+(X\,^1\Sigma^+)$

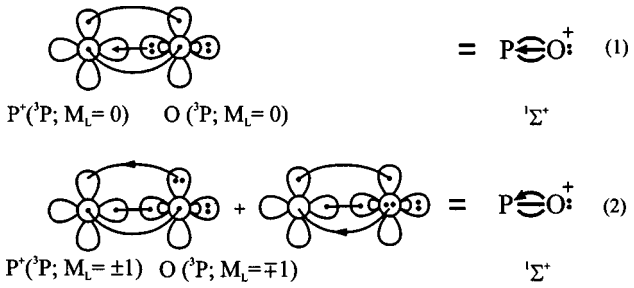
The experimental ionization energies (I.E.) of the P and O atoms are 11.0 and 11.614 eV respectively.[71] Assuming that the ground state of the PO^+ species correlates to the ground states of the atoms, there are two ways of forming a

TABLE III. Equilibrium energies, bond distances, dissociation energies, spectroscopic constants, dipole moments, ionization energies (I.E), and electron affinities (E.A.) of PO ($X\ ^2\Pi$) at the MRCI, RCCSD(T), C-MRCI, and C-RCCSD(T)/aug-cc-pV6Z level of theory[a] (experimental values from Table I).

	MRCI	RCCSD(T)	C-MRCI[b]	C-RCCSD(T)[b]	Experiment
E (E_h)	−416.024 61	−416.059 14	−416.224 68	−416.281 58	
E+Q (E_h)[c]	−416.0544		−416.269 68		
E−CBS (E_h)[d]	−416.0270				
r_e (Å)	1.479 3	1.479 5	1.468 5	1.475 0	1.476 37[e]
					1.476 373 55(10)[e]
r_e−CBS (Å)[d]	1.478 6				
D_e (kcal/mol)	137.76[f]	142.04	138.80	144.18	141.80[g,h]–144.2[g,i]
D_e+Q (kcal/mol)[c]	141.04		142.68		
D_e−CBS (kcal/mol)[d]	138.10		139.62		
ω_e (cm^{-1})	1226.56	1238.22	1271.70	1247.4	1233.34[j]
ω_e−CBS (cm^{-1})[d]	1228.68				
$\omega_e x_e$ (cm^{-1})	6.73	5.75			6.56[j]
B_e (cm^{-1})	0.730 32	0.730 18	0.735 86	0.734 60	0.733 23[e]
α_e (cm^{-1})×10^{-3}	5.53	5.52			5.474 2[k]
$\overline{D_e}$ (cm^{-1})×10^{-6}	1.09	1.05			1.04
A_e (cm^{-1})[l]	213.98				224.01±0.01[j]
μ (D)	1.874		1.788		1.88±0.07[m]
μ−CBS (D)[d]	1.875				
I.E. (eV)	7.933	8.358	7.784	8.351	8.39[n]
I.E.+Q (eV)[c]	8.28		8.18		
E.A. (eV)	0.722	1.102	0.644	1.082	1.09±0.01[o]
E.A.+Q (eV)	0.94		0.89		

[a]See Table I for symbol explanation.
[b]Including the $2s^2 2p^6$ e^- of P in the correlation treatment.
[c]Including the Davidson (+Q) correction.
[d]Complete basis set limit, see the text.
[e]Reference 46.
[f]Including the BSSE correction, this value reduces to 137.60 kcal/mol, see Table VI.
[g]$D_e = D_0 + \omega_e/2 - \omega_e x_e/4$.
[h]Minimum D_0 value, Ref. 42.
[i]Maximum D_0 value, Ref. 47.
[j]Reference 34.
[k]Reference 51.
[l]Spin–orbit coupling constant/A5Z-g-h, see Table VI.
[m]Reference 49.
[n]Reference 43.
[o]Reference 37.

$^1\Sigma^+$ state as is shown schematically from the following vbL icons:

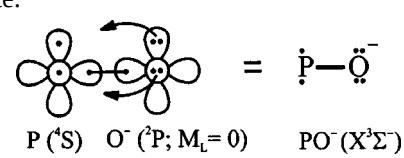


Already at the interatomic distance of 6.0 bohr, the CASSCF Mulliken distribution (P/O) is $3s^{1.963}3p_z^{0.075}3p_x^{0.982}3p_y^{0.982}/2s^{2.0}2p_z^{1.967}2p_x^{1.0}2p_y^{1.0}$, and it shows that the bonding is represented by scheme (1). At equilibrium ($r=2.70$ bohr) the dominant MRCI configuration is $|X\ ^1\Sigma^+\rangle \simeq 0.93|5\sigma^2 6\sigma^2 7\sigma^2 2\pi_x^2 2\pi_y^2\rangle$ with corresponding populations $3s^{1.81}3p_z^{0.84}3p_x^{0.54}3p_y^{0.54}/2s^{1.81}2p_z^{1.52}2p_x^{1.36}2p_y^{1.36}$, clearly pointing to scheme (1) and the formation of a genuine triple bond, a dative σ from O to P and two π bonds.

From Table IV we can see that at the C-MRCI or C-RCCSD(T) level the bond length is in complete agreement with the experimental value while the C-MRCI D_e is slightly overestimated. Interestingly, the RCCSD(T) D_e value is the average of the two existing experimental values: (192.3 +195.9)/2=194.10 kcal/mol. At this point we would like to mention that PO^+ is isovalent to CO ($X\ ^1\Sigma^+$) and isoelectronic and isovalent to SiO($X\ ^1\Sigma^+$). The spectroscopic parameters[40] of the latter are in striking agreement with those of PO^+, with small variances pertaining to the size difference between the P and Si atoms: $r_e=1.509\,739$ Å, $D_e=192.25$ kcal/mol, $\omega_e=1241.56\ cm^{-1}$, and $\omega_e x_e=5.966\ cm^{-1}$.

C. $PO^-(X\ ^3\Sigma^-)$

One could think that PO^- is a closed shell system since it is formed by adding one electron to the doublet ground state of PO. However, the much higher electron affinity of O (1.461 eV),[72] in comparison to that of P (0.75 eV),[73] dictates the formation of a different and unique bonding picture in the ground state:



Indeed, this is the case, resulting to a $^3\Sigma^-$ ground state and a remarkably strong "formal" σ bond ($D_e=135-136$ kcal/mol, see Table V). The above given picture

TABLE IV. Equilibrium energies, bond distances, dissociation energies, spectroscopic constants of PO^+ ($X\ ^1\Sigma^+$) at the MRCI, RCCSD(T), C-MRCI, and C-RCCSD(T)/aug-cc-pV6Z level of theory[a] (experimental values from Table I).

	MRCI	RCCSD(T)	C-MRCI[b]	C-RCCSD(T)[b]	Experiment
E (E_h)	−415.733 08	−415.752 00	−415.938 63	−415.974 70	
$E+Q$ (E_h)[c]	−415.750 2		−415.969 0		
r_e (Å)	1.430 1	1.428 7	1.425 0	1.424 7	1.424 99[d]
D_e (kcal/mol)	193.07	191.67	196.33	194.10	192.3±0.23,[e,f] 195.9[e,g]
D_e+Q (kcal/mol)[c]	193.1		194.5		
ω_e (cm^{-1})	1411.3	1413.3	1432.5	1424.5	1411.5(3)[d]
$\omega_e x_e$ (cm^{-1})	7.88	7.49			7.11[d]
B_e (cm^{-1})	0.781 39	0.782 91			0.787 04[d]
α_e (cm^{-1})×10^{-3}	5.31	5.28			
$\overline{D_e}$ (cm^{-1})×10^{-6}	1.13	0.96			

[a]See Table I for symbol explanation.
[b]Including the $2s^2 2p^6\ e^-$ of P in the correlation treatment.
[c]Including the Davidson (+Q) correction.
[d]Reference 50.
[e]$D_e = D_0 + \omega_e/2 - \omega_e x_e/4$.
[f]Reference 43, but ω_e, $\omega_e x_e$ values from Ref. 50.
[g]Reference 40.

TABLE V. Equilibrium energies, bond distances, dissociation energies, spectroscopic constants of PO^- ($X\ ^3\Sigma^-$) at the MRCI, RCCSD(T), C-MRCI, and C-RCCSD(T)/aug-cc-pV6Z level of theory[a] (experimental values from Table I).

	MRCI	RCCSD(T)	C-MRCI[b]	C-RCCSD(T)[b]	Experiment
E (E_h)	−416.051 13	−416.099 62	−416.248 35	−416.321 34	
$E+Q$ (E_h)[c]	−416.088 9		−416.302 4		
r_e (Å)	1.535 4	1.533 8	1.529 1	1.532 2	1.54±0.01[d]
D_e (kcal/mol)	131.49	134.32	132.71	136.00	134.8[d,e]
D_e+Q (kcal/mol)[c]			135.2		
ω_e (cm^{-1})	1057.8	1058.9	1052.4	1056.3	1000±70[d]
$\omega_e x_e$ (cm^{-1})	6.08	5.75			
B_e (cm^{-1})	0.677 95	0.676 35			0.699[d]
α_e (cm^{-1})×10^{-3}	5.63	6.00			
$\overline{D_e}$ (cm^{-1})×10^{-6}	1.12	1.04			

[a]See Table I for symbol explanation.
[b]Including the $2s^2 2p^6\ e^-$ of P in the correlation treatment.
[c]Including the Davidson (+Q) correction.
[d]Reference 37.
[e]$D_e = D_0 + \omega_e/2 - \omega_e x_e/4$, but using the calculated average ω_e and $\omega_e x_e$ values.

TABLE VI. Total energies (E_h), bond distances r_e (Å), dissociation energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), dipole moments μ (D), spin–orbit coupling constant A_e (cm^{-1}), basis set superposition errors BSSE (kcal/mol), and complete basis set limits CBS of the PO ($X\ ^2\Pi$) molecule at the MRCI, MRCI-BSSE corrected, and C-MRCI/aug-cc-pVnZ, n=D, T, Q, 5, 6 level.

n	Method	$-E$	r_e	D_e	ω_e	μ	A_e[a]	BSSE
	MRCI	415.886 434	1.5342	113.70	1114.0	1.944	213.58	
D	MRCI-BSSE	415.881 304	1.5379	110.48	1103.8	1.953		3.212
	C-MRCI	415.893 654	1.5344	114.66		1.945		
	MRCI	415.981 964	1.4962	129.56	1199.9	1.884	213.32	
T	MRCI-BSSE	415.979 811	1.4977	128.21	1195.4	1.888		1.349
	C-MRCI	416.019 980	1.4932	130.79		1.964		
	MRCI	416.010 593	1.4860	134.69	1215.5	1.881	213.55	
Q	MRCI-BSSE	416.009 589	1.4866	134.06	1213.6	1.882		0.630
	C-MRCI	416.062 194	1.4811	137.70		1.886		
	MRCI	416.021 132	1.4806	137.04	1224.4	1.875	213.98	
5	MRCI-BSSE	416.020 681	1.4809	136.75	1223.4	1.875		0.283
	C-MRCI	416.170 686	1.4769	138.15		1.819		
	MRCI	416.024 610	1.4793	137.76	1226.6	1.874		
6	MRCI-BSSE	416.024 370	1.4795	137.60	1226.1	1.874		0.151
	C-MRCI	416.224 683	1.4685	138.80		1.788		
	MRCI	416.027 0	1.4786	138.1	1228.7			
CBS	MRCI-BSSE	416.026 8	1.4787	138.0	1228.4	1.875		
	C-MRCI			139.6				

[a]Using the uncontracted basis sets, while removing the g and the g, h atomic functions from the A4Z and A5Z sets, respectively.

is corroborated by the dominance of a single CASSCF configuration, $|X\,^3\Sigma^-\rangle \simeq 0.98|5\sigma^2 6\sigma^2 7\sigma^2 2\pi_x^2 2\pi_y^2 3\pi_x^1 3\pi_y^1\rangle$, and the corresponding Mulliken atomic distribution (P/O):

$$3s^{1.85}3p_z^{0.75}3p_x^{1.29}3p_y^{1.29}3d_{z^2}^{0.06}3d_\pi^{0.18}/2s^{1.88}2p_z^{1.48}2p_x^{1.61}2p_y^{1.61}.$$

Overall, 0.42 e^- are transferred from the O^- to the P atom: 0.34 e^- through the σ frame from P to O^- and 0.76 e^- from O^- to P via the π system.

Figure 1 shows the complete PEC of PO^- ($X\,^3\Sigma^-$) at the MRCI level, while numerical findings are reported in Table V. We can claim that the ''true'' bond distance is 1.532–1.534 Å as compared to the experimental value of 1.54 ± 0.01 Å.[37] The values of the remaining calculated properties ($D_e, \omega_e, \omega_e x_e$) both with the multireference and the coupled cluster methods, follow the pattern already discussed. Note that the PO^- system is isoelectronic and isovalent to PF ($X\,^3\Sigma^-$), which has $D_e = 105 \pm 6.9$ kcal/mol[74] and $r_e = 1.58933$ Å.[75] The smaller binding energy of PF by about 30 kcal/mol and its larger interatomic distance by 0.055 Å as compared to those of PO^-, is attributed to the complete localization of the p_π electrons of the former on the F atom (I.E.=17.42 eV),[71] resulting to a pure σ P–F bond, as contrasted to PO^- where a flow of electrons from O^- (I.E. =1.461 eV) [72] to P introduces partial π bonding character.

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